

Glassy Carbon Electrode Modified by Multi-walled Carbon Nanotubes for Detection Platform of Organochlorine Pesticides

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Abstract

Current detection methods for pesticide monitoring include spectrophotometric techniques which are time consuming and costly due to expensive instrumentation and complicated procedures. Electrochemical analysis techniques provide for portable, low cost and high speed pesticide detection. However, the direct usage of an electrode in detecting chlorobenzene amperometrically requires a high detecting voltage and usually results in low sensitivity and poor selectivity. In this study, NaOH was used to re-sensitize and improve the adhesion of multi-walled carbon nanotubes (MWCNTs) to the electrodes. This increased the electron transfer signalling strength, resulting in greater sensitivity and reproducibility. Modified electrodes coated with five layers of MWCNTs had a short detection time of 26 s using cyclic voltammetry. The modified electrodes have significantly improved in sensitivity 400% as compared to unmodified electrodes. Moreover, after 100 consecutive uses, the detection capability continued to provide excellent results. The limit of detection of the modified electrode was 0.1 mgL⁻¹ of chlorobenzene with a fast response time of 2 ms. Our results have indicated that the modified electrode is suitable for rapid organochloride pesticide determination.

Keywords

Chlorobenzene; Electrode Modification; Multi-walled Carbon Nanotubes; Organochlorine Pesticide

Introduction

Chlorobenzene is a widely used toxic biological substance in organochlorine pesticides due to its long half-life. Currently, organochlorine pesticides that have low disappearance from the soil and high toxicity are banned from use. However, due to their extensive use in the past, there remain toxic residues in the environment. Organochlorine pesticides bioaccumulate easily, causing nerve damage and contributing to carcinogenic risks. Hence, the monitoring of organochlorine pesticide residues in the environment and crops are of great public interest. Presently,

techniques such as thin layer chromatography (TLC), high performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS) and colorimetry are used to detect pesticide residues (Hogendoorn et al.; Akbal et al.; Mallat & Barcelo). In 2001, Gennearo indicated that though HPLC has high levels of sensitivity and selectivity, the process takes 24 to 36 h, associated with high maintenance costs and only capable of analyzing high purity substances. Thus, there is an urgent need for the development of a rapid, accurate and cost effective detection platform.

Electrochemical analysis is a forward-looking technique with great opportunity for future advancement in the monitoring of pesticides. The resulting peak voltage and current from electrochemical analysis provides insight into the composition of pesticides. Its three-electrode configuration allows portability, fast detection and low cost. Moreover, the technique does not require specialized personnel. The modification of electrodes allows higher levels of sensitivity and selectivity. However, during the electrochemical reaction, the electron transfer is slow, which can result in the deposition of organic materials and the passivation of the electrode. Consequently, this affects the sensitivity and reproducibility of the electrochemical system. Thereby, the use of electrochemical voltammetry system for detection of chlorobenzene is not ideal. Currently, some researches have examined electrochemical techniques in the detection of chlorobenzene (Huang et al.; Salimi et al.; Manisankar et al.). As such, further research and development remains to be performed.

Multi-walled carbon nanotubes (MWCNTs) have been reported to have excellent conductivity, and considered to be an attractive material for use in metal or semiconductors (Leghrib et al.; Tekleab et al.). As a result of their large surface area, MWCNTs have great

adhesion effects and promote faster electron transfer velocity during the electrochemical reaction (Yang et al.). Hence, this option is suitable for the development of electrochemical sensors. Additionally, because MWCNTs possess strong mechanical structures, high electrical conductivity and chemical stability, the number of deposits on the sensors during the electrocatalytic process and the electrolytic reaction is reduced (Wang et al.; Sun et al.; Musameh; Zare & Nasirizadeh). Subsequently, MWCNTs are also used to modify bare glassy carbon electrodes in order to improve the electron transfer signalling speed. At the same time, this reduces over-voltage signal generation beyond the scope of the potential range (Zare & Nasirizadeh). Presently, after the modification of the electrodes with MWCNTs, the sensitivity is improved and the minimum measurement concentration is required before conductive compositions are detectable (detection limit) lowered to $\mu\text{g L}^{-1}$ level. However, the MWCNTs are prone to peeling off from the electrodes, resulting in unstable current/voltage peaks. This significantly affects experimental results. Henceforth, methods to improve electrochemical detection speed and organochlorine pesticides sensors are of utmost need.

This study aims to increase electrochemical analysis efficiency by using MWCNTs modified glassy carbon electrode to detect chlorobenzene in organochlorine pesticides. The detection of chlorobenzene follows from the principal that peak current will be detected from the oxidation of chlorobenzene after the electrical potential was applied to test organochlorine pesticide. To reduce the shredding effect of MWCNTs from glassy carbon electrodes (GCEs), re-sensitization of GCEs by either a sulphuric acid (H_2SO_4) or a sodium hydroxide (NaOH) solvent to strengthen the adhesion has been examined. Consequently, by improving MWCNTs modification of GCEs, the ability of the electrochemical analysis system to test organochlorine pesticides was investigated. Making a breakthrough against past difficulties to maintain adhesion of MWCNTs to GCEs, a greater detection limit and better test results were achieved, creating a better platform for rapid detection in the future.

Materials and Methods

Reagents

Chlorobenzene, acetonitrile, sodium dodecyl sulfate (SDS), 95% ethanol, potassium chloride, sulphuric acid, and sodium hydroxide were purchased from

Katayama Ltd. (Osaka, Japan). The phosphate buffer solution (PBS) was purchased from Sigma-Aldrich Company (Saint Louis, USA). The MWCNTs (C tube-015H, Diameter: 10~20 nm, Length > 1 μm , Purity > 98%) were purchased from Global Innovation Business Co., Ltd. (Taiwan). The 0.3 μm and 0.05 μm alumina slurry (Al_2O_3) and micro velvet fabric were purchased from BASi Corporation (Japan) to scrub residue deposits off the electrodes.

Apparatus

The electrochemical analyser was purchased from Jia Yu Enterprise Co., Ltd. (Taiwan). Three-pole electrodes: GCE (MF-2052), aqueous silver-silver chloride (Ag/AgCl) reference electrode (RE1B) and a platinum wire counter electrode were purchased from BASi Corporation (Japan). The ultrasonic sink (3510-DTH) was purchased from Bransonic (Taiwan).

The Redox Potential of Chlorobenzene

Cyclic voltammetry was used to exploit the redox electrical potential of chlorobenzene for subsequent experiments used to determine chlorobenzene amounts in organochlorine pesticides. By adjusting the high voltage between 3 to 5 V and low voltage at between -3 to -5 V, with a velocity of 0.1 to 5 V/s and a chlorobenzene concentration of 0.2 mg L^{-1} , the peak current and peak potential of chlorobenzene were determined.

Electrode Pre-treatment

In order to reduce possible current interference, the GCEs were scrubbed with a micro velvet fabric for 20 min followed by sonication in 95% ethanol for 15 min to remove residues deposited on the GCE surface. In addition, to allow better adsorption of MWCNTs to the GCE, providing for increased the amount of GCE modification and sensitivity, the GCE was separately pre-treated with either a 0.5 M H_2SO_4 or a 0.5 M NaOH solution. Amperometric i-t curves were used to re-sensitize the GCE that was in either H_2SO_4 or NaOH by applying a 1.2 V voltage for 30 min. Further, linear sweep voltammetry (LSV) was used to investigate whether the pre-treatment of GCE with H_2SO_4 or NaOH produced the most obvious electrical potential peaks to determine the best pre-treatment solution for the GCE.

Preparation of MWCNTs Modified GCE

5 mg of the MWCNTs was suspended in 50 mL of a 0.1 M SDS solution, the weight ratio of MWCNTs and

SDS was 3.45:1, and later sonicated for 24 h in order to mix uniformly. Sequentially, 5 μL of the solution was applied onto the GCE in droplets, and then placed in an oven at 50°C to evaporate the solution. Successively, distilled deionized water (ddH_2O) was used to wash the GCE surface to remove the SDS. Once dried, the GCE was considered modified with the MWCNTs. The effect of different number layers of MWCNTs coated on GCE was investigated with regard to reproducibility, sensitivity and detection limit. During the detection process, solvent consisted of 50% acetonitrile and 10mM KCl was used.

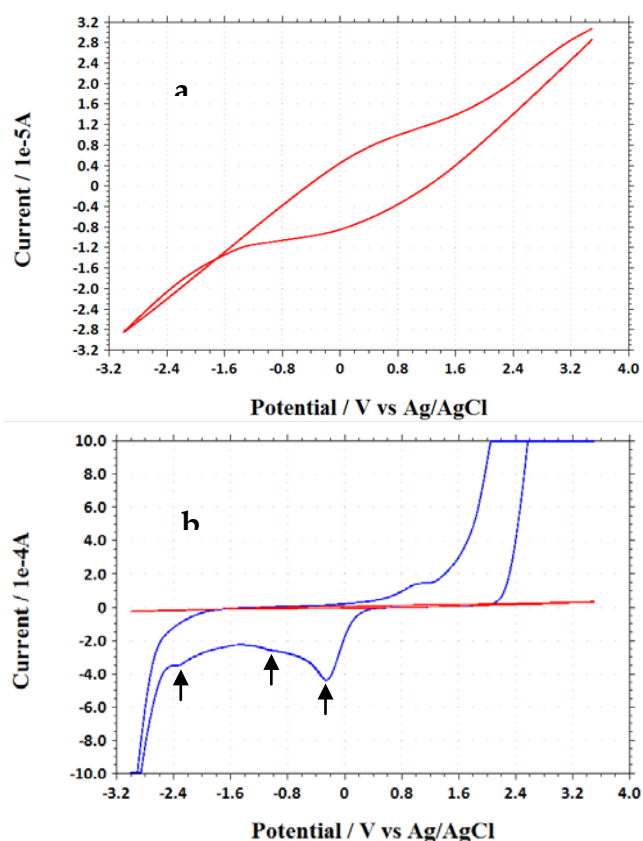


FIG. 1 (A) CYCLIC VOLTAMMETRY OF MODIFIED ELECTRODE AT 50% ACETONITRILE, 10 MINIMOLAR KCL (B) BLUE CLOSED LOOP INDICATES THE CURRENT-POTENTIAL CURVE OF CHLOROBENZENE AT 0.2 MINIGRAM PER LITER IN 50% ACETONITRILE, 10MINIMOLAR KCL

Results and Discussion

Studies have often used 100% acetonitrile as their reference background solvent in electrochemical analysis (Jalil et al.). However, some studies have suggested that 50% acetonitrile solvent is the most appropriate (Peverly et al.). Given that pure acetonitrile is highly toxic to the experiment operator and the organic material is poorly soluble in ddH_2O , 50% acetonitrile solvent was considered the most suitable reference background solvent in this study

(Peverly et al.). Additionally, the use of 50% acetonitrile solvent did not significantly affect the cyclic voltammetry results of chlorobenzene. Figure 1a shows the cyclic voltammetry diagram of modified electrode in background solution when detecting of chlorobenzene. There are no anodic and cathodic peaks observed at the background solution. Given a range of voltage from +3.5 to -3 V, at a scan rate of 0.5 V/s and 0.2 mgL^{-1} chlorobenzene was added into the background solution. An oxidation potential peak was observed at +1.2 V (Figure 1b). The oxidation potential reflects the oxidation reaction of chloride. Reduction potential peaks were also observed at -0.23, -1.1 and -2.35 V. However, as shown in Figure 1b, the reduction potential wavefronts were susceptible to free electron interference, providing a poor indication of the actual chlorobenzene reduction potential. Accordingly, +1.2 V was used in this study as an indicator to determine chlorobenzene in organochlorine pesticides.

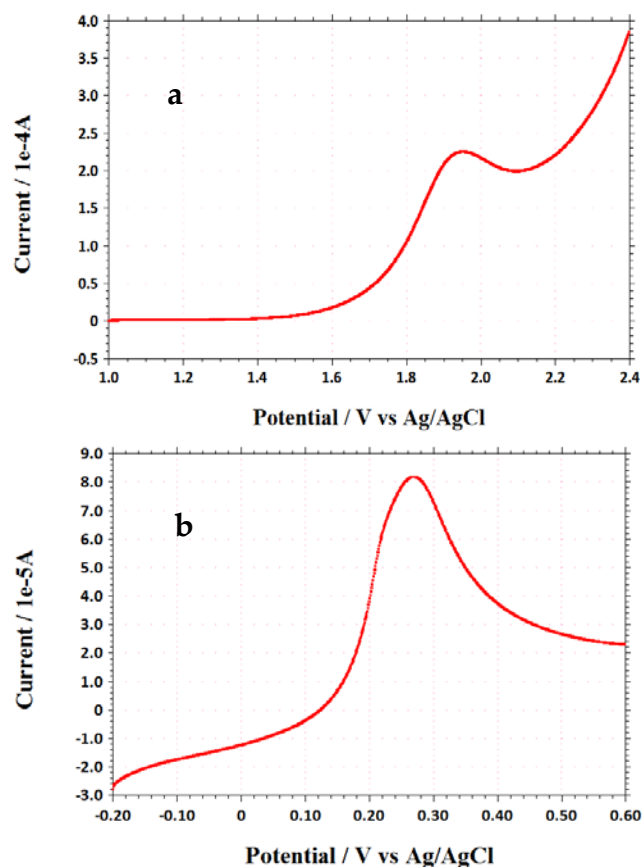


FIG. 2 THE LSV DETECTION CURVES OF GCE IN 50% ACETONITRILE, 10MINIMOLAR KCL. (A) REPRESENT LSV RESULTS OBTAINED FROM GCE PRE-TREATED WITH THE H_2SO_4 SOLUTION. (B) REPRESENT LSV RESULTS OBTAINED FROM GCE PRE-TREATED WITH THE NaOH SOLUTION. THEIR SCAN RATE WAS 0.1VOLTAGE PER SECOND

H_2SO_4 and NaOH solution were examined as purposeful pre-treatment processes to reduce the shredding of materials from the GCEs during

organochlorine pesticide measurement. After pre-treatment of the GCEs with H_2SO_4 and NaOH , the GCEs showed increased adhesion effect allowing better attachment of special functional groups. The increased adhesiveness between the MWCNTs and GCEs was indicated by the results obtained from the LSV (Figure 2). However, at +2.1 to +2.4 V, the current produced by the GCEs pre-treated with 0.5 M H_2SO_4 was easily interfered by other subsequent electrons reaching the electrodes (Figure 2a). This suggested that LSV results obtained from H_2SO_4 can be flawed. On the contrary, Figure 2b shows that GCEs pre-treated with NaOH produce apparent an oxidation current peak. Therefore, to enhance organochlorine pesticides tests, NaOH was used in subsequent steps to pre-treat the GCEs.

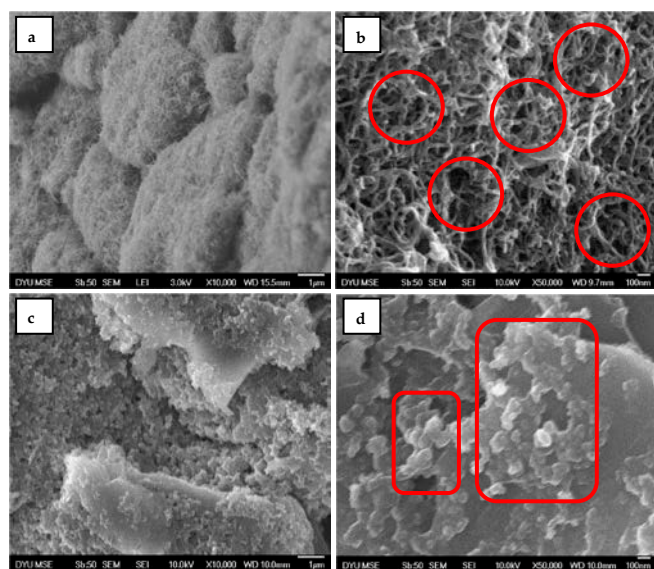


FIG. 3 SEM IMAGE OF GCE MODIFIED MWCNTS AT DIFFERENT MAGNIFICATIONS. (A) AND (C) WERE AT 10KX. (B) AND (D) HAD A MAGNIFICATION OF 50KX. THE GCE WAS PRE-TREATED WITH A 0.5M NaOH SOLUTION

The MWCNTs were suspended in an SDS solution (weight ratio is 3.45:1) prior to coating onto the GCEs surface. The surface morphology of the GCEs modified MWCNTs (MWCNT-GCEs) was investigated using a scanning electron microscope (SEM) at 10 kX. The results confirmed the presence of MWCNTs on the GCEs surface (Figure 3a). Upon magnification to 50 kX, winding shaped MWCNTs were observed (Figure 3b). On average, the MWCNTs had a diameter of 40 nm. Furthermore, the MWCNTs structure resulted in a porous GCEs surface. This suggested that the porous structure may increase chlorobenzene adhesion, and enhance electrochemical analysis and electrical potential detection. Moreover, it has the potential to increase the sensitivity of GCEs. After organochlorine pesticide assessment with MWCNT-GCEs, SEM investigation

demonstrated the adhesion of chlorobenzene onto MWCNT-GCEs (Figure 3c and 3d). At a higher magnification (50kX), the chlorobenzene was observed to crowd around the MWCNT-GCEs surface (Figure 3d). Further investigation (Figure 4) supported the hypothesis that when more chlorobenzene are attached to the MWCNT-GCEs, the greater the electrical potential response is to a certain degree of MWCNTs coating.

Further analysis into the sensitivity of MWCNT-GCEs with increasing MWCNTs coating layers revealed that five coats of MWCNTs on GCEs produced the best current with an average response of 3.4A given 100 consecutive chlorobenzene detections (Figure 4). The reason for this is such that the MWCNT-GCEs required up to 5 MWCNTs coatings before the best sensitivity level was reached. However, after five layers, the MWCNTs have become overly bundled together resulting in a reduced conductive surface area around the structure space of the MWCNTs. The reduced surface area outweighs the benefit of MWCNTs sensitivity.

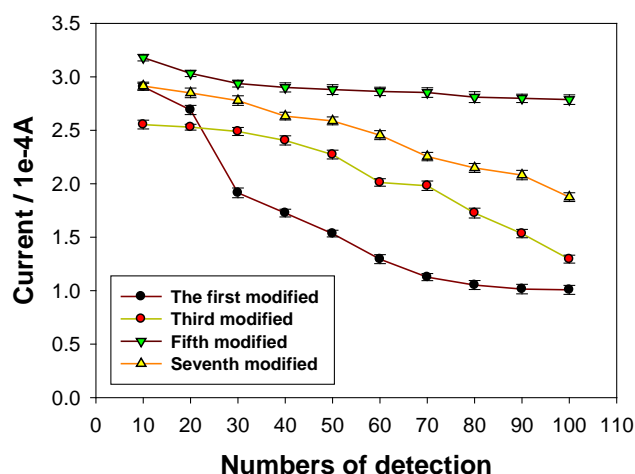


FIG. 4 THE REPRODUCIBILITY OF THE MWCNTS-GCES GIVEN DIFFERENT AMOUNT OF MWCNTS COATING LAYERS. IN LSV AT 0.2MINIGRAM PER LITER CHLOROBENZENE

A comparison between the GCEs modified MWCNTs and unmodified GCEs, demonstrated that at 1.2V five MWCNT coated GCEs had a greater level of sensitivity (4.38A) than non-modified GCEs (1.08A) at 1.2 voltage (Figures 5a and 5b, respectively). The detection sensitivity of the chlorobenzene of GCEs was increased four-fold. This heightened sensitivity may be a result of chain conductive polymers covering the surface of the carbon nanotubes, which may strengthen the electric transmission capability. This experiment has attested that MWCNT-GCEs utilisation in an electrochemical system is a forward-looking development platform for the detection of organochlorine pesticides

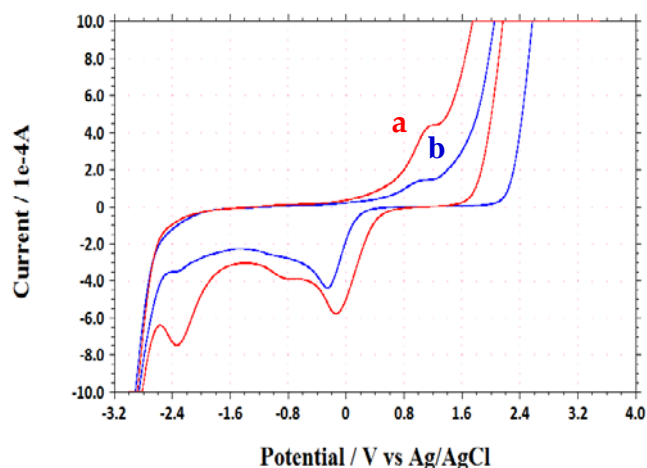


FIG. 5 CYCLIC VOLTAMMETRY COMPARISON OF FIVE LAYERS MWCNTS WITH NaOH PRE-TREATED AND MODIFIED (A) OR NON-MODIFIED (B) GCEs CHLOROBENZENE DETECTION SENSITIVITY

The detection limit of chlorobenzene in organochlorine pesticides was also examined. The range of chlorobenzene concentration used in this study (0.2 to 0.04 mgL^{-1}) was based on a reference from the Taiwan Department of Health, Food and Drug Administration (report number: 1021300623). Presently, the lowest concentration detectable by other technologies is 0.05 mgL^{-1} . Here, no significant peaks were observed at a concentration below 0.1 mgL^{-1} chlorobenzene, which suggested that the MWCNT-GCEs electrochemical system had a detection limit of 0.1 mgL^{-1} (Figure 6). In future study, a pesticide selective membrane may be adapted to the electrochemical system. This might enhance the specificity for organochlorine pesticide examination and lower the detectable concentration limits.

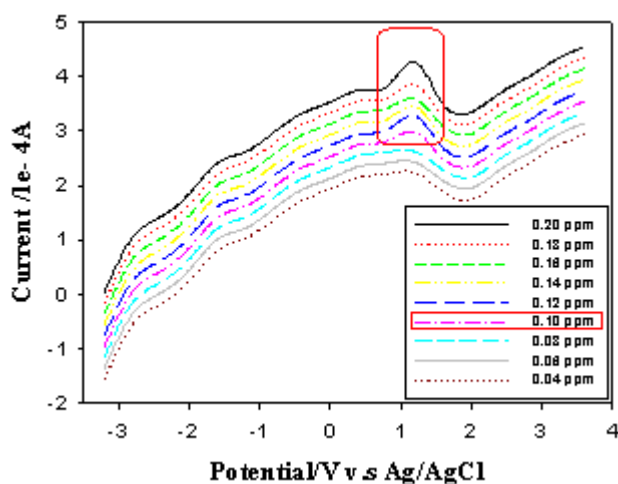


FIG. 6 DETECTION LIMIT OF CHLOROBENZENE CONCENTRATIONS USING MWCNTS-GCEs WITH NaOH PRE-TREATMENT AND FIVE LAYERS OF MWCNTs IN LSV

Conclusions

In this study, NaOH was used as a re-sensitizer to pre-

treat the GCE and enhance the adhesion of MWCNTs onto the GCE. Furthermore, with five added layers of MWCNTs, the MWCNT-GCEs had a four-fold increase in sensitivity and a high degree of reproducibility. Under these conditions, the detection time only took 26 s and the lowest detectable chlorobenzene concentration in organochlorine pesticides was 100 mgL^{-1} . In comparison to other detection platform of organochlorine pesticides available in the market, rapid screening of pesticides residue was markedly improved in this MWCNT-GCEs system.

This research platform may be developed into commodity-typed portable mini sensors and disposable sensing chips in the future. Moreover, this research differed from the more expensive and time consuming plasma vapour deposition method used to coat MWCNTs onto GCEs. Thus, the production time and cost is greatly reduced using our revised research technique. The outlook of this improved technique is bright, as it provides great opportunities for governmental health units and agro-industrial production suppliers. During the import and export of crops and products, the use of this platform in regular custom checks allows rapid pesticide detection, essentially giving this platform a possible global market potential.

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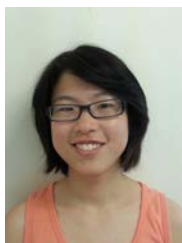
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